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Fabrication and properties of graphene-coated polypropylene hollow fiber membranes

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ABSTRACT

Graphene(GE) was employed to increase the hydrophobic property of polypropylene (PP) hollow fiber membranes and hot solvent treatment was used to strengthen the combination of GE with PP hollow fiber membrane. Dimethylbenzene(DMB) as the solvent was used at different temperatures in this study. The stacked and folded GE sheets on the GE-coated PP hollow fiber membranes was observed using a scanning electron microscopy (SEM).In addition, the water contact angle and water entry pressure increased significantly compared to untreated PP hollow fiber membrane. The process of GE-coated PP hollow fiber membrane used for kerosene-water separation was measured with a laboratory-scale continuous setup under –0.09MPa.It demonstrated that the GE-coated PP hollow fiber membranes can achieve continuous oil-water separation and exhibits good durability and reusability. This approach provides a workable method of preparing GE functionalized PP hollow fiber membrane.

Keywords: Graphene; Hydrophobicity; Continuous oil-water separation; PP hollow fiber membranes

1. Introduction

Oil-water mixture separation has been a worldwide problem accompanying the development of industry and society. Oily wastewater has caused serious pollution involving the hydrosphere, the biosphere and the atmosphere. Moreover, oils are non-renewable resource and most of them can be reused again after recycle. It is necessary and urgent for oil recycling in the treatment of oily wastewater. Currently, oil spills are removed from water surface by a variety of methods, such as mechanical collection [1], chemical dispersants [2], bioremediation [3], and absorbent materials [4–6].

The earliest oil adsorbents are mainly natural materials with porous structure, including activated carbon, bentonite [7], wheat straw, rice straw and cotton grass fiber [8]; these materials are low-cost, however, showing low adsorption capacity and poor oil-water selectivity. Several oil-adsorptive polymer materials, including polypropylene non wovens [9] and polyurethane foam [10], are used in preliminary oil-water separation. Although these materials can separate oil-water mixtures, it is still difficult to continuously deal industrial oily wastewater and recycle oil. It cannot afford the water treatment in terms of separation efficiency and effluent quality.

Membrane separation has gradually become a powerful and prior technology for oil-water separation in last decades [11,12].Compared to conventional treatment methods,it can be currently utilized for oily wastewater treatment, showing high oil removal efficiency,low energy cost, no chemical additives, small space occupancy and compact design [13–15]. Using ultrafiltration processes, Ebrahimi et al. [16] treated refinery oily wastewater and reported 95% oil removal.

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GE as a single atom-thick sheet composed of sp2 hybridized carbon atom showed highly hydrophobic [17]. The GE based materials have been employed for oil adsorption and oil-water separation, such as carbon aerogel [18], spongy GE [19] and GE-based sponge [20]. Sun et al. [18] prepared carbon aerogel via reducing the graphene oxide-carbon nanotubes mixture, which showed high adsorption capacity for kinds of oils. Bi et al. [19] prepared spongy graphene via reducing the graphene oxide air gel thermally and its oil adsorption capacity up to 20 to 80 g/g. Nguyen et al. [20] prepared GE-based sponge via dip-coating, which were demonstrated as efficient absorbents for a broad range of oils and organic solvents with high oil-water selectivity, good recyclability, low self-weight, and excellent oil adsorption capacity approaching to 165 g/g. Polypropylene (PP) hollow fiber membrane prepared by TIPS has excellent properties, including natural hydrophobic property, low cost, good mechanical property and chemical stability [21]. However, no work seems to be reported on the functionalized PP hollow fiber membrane with GE which was used for oil-water separation until recently.

In this study, GE-coated PP hollow fiber membrane consisting of PP matrix membrane and GE coating layer was obtained by the method of dead end filtration and hot solvent treatment. GE was employed to increase the hydrophobic property of PP hollow fiber membranes and hot solvent treatment was used to strengthen the combination of GE with PP hollow fiber membrane. The performance of GE-coated PP hollow fiber membrane on continuous oil-water separation was investigated through a laboratory-scale continuous setup under –0.09MPa.

2. Experimental

2.1. Materials

PP hollow fiber membrane (prepared by TIPS; average pore size, ~0.12 μm; porosity, ~50.93%) was purchased from Tianjin Haizhihuang Technology Co., Ltd.GE (KNG-G5; dark powder; thickness, ~5 nm; flake diameter, 0.1~5 μm) was purchased from Xiamen Knano Graphene Technology Co., Ltd. Kerosene was obtained from Tianjin Kailida Chemical Co., Ltd. Ethanol were purchased from Tianjin Wind Ship Chemical Technology Co., Ltd. DMB were obtained from Tianjin Guangfu Fine Chemical Research Institute. All chemicals are directly used without further purification.

2.2. Hollow fiber membrane preparation

GE and ethanol were mixed after ultrasonic dispersion 30 min, and form a uniform system. The PP hollow fiber membrane was packed into membrane module, and immersed into the above GE dispersion. PP hollow fiber membrane was vacuum pumped for a certain time (15 s, 30 s, 45 s, 60 s, 120 s) by the dead end filtration under –0.09 MPa, the product was labelled as M1, M2, M3,M4, M5, respectively. A thin GE coating layer on the PP hollow fiber membrane surface was formed. After that, the GE coating PP hollow fiber membranes were immersed into the hot solvent DMB for 5 s at different temperatures (115°C, 120°C, 125°C). The membrane module was totally dried for 2 h until solvent evaporation. The GE-coated PP hollow fiber membrane was prepared. Meanwhile the original PP hollow fiber membrane without GE coating was labelled as M0. Samples were labeled *X*-*Y*, where *X* and *Y* indicate the value of different temperatures and the type of the GE coating PP hollow fiber membranes (M1, M2, M3, M4, M5), respectively.

2.3. Membrane characterizations

2.3.1. The coating amount of GE on the GE-coated PP hollow fiber membrane surface

The coating amount of GE on the GE-coated PP hollow fiber membrane surface by the dead end filtration at different time was calculated by the following Eq. (1):

$$W = (w_2 - w_1)/ S \tag{1}$$

where w_1 is the weight of dry membrane module, w_2 is the weight of GE coating membrane was totally dried for 10 min at 70°C, S is the effective coverage of GE (m^2).

2.3.2. Scanning electron microscope (SEM)

The morphology of surface and cross-section of GE-coated PP hollow fiber membrane was observed by a scanning electron microscope (TM3030, Hitachi, Japan). Then, the membranes were broken for cross-section observation after freezing by liquid nitrogen for 10–15 s. Samples were all gold sputtered before testing.

2.3.3. Bubble pore size and porosity

The bubble pore size of each sample were determined by using the capillary flow porometer (Porous Materials Inc., USA), and the values were calculated from the pressure of the gas flow.

Gravimetric method was used for assessing the porosity which calculated the weight of liquid immersed in the membrane pores. N-butyl alcohol was used as the wetting liquid. The porosity (ε) was calculated by Eq. (2)

$$\varepsilon(\%) = (W_1 – W_2)/[(\pi/4)\ (D^2 – d^2)\ l\rho] \times 100\% \tag{2}$$

where D is the outer diameter (cm); d is the inner diameter (cm); l is the length of sample membrane (cm); ρ is the n-butyl alcohol density (ρ = 0.81 g/ml); W_1 is the weight of wet membrane (g), and W_2 is the weight of dry membrane (g).

2.3.4. Membrane surface wetting properties

The surface wetting properties of GE-coated PP hollow fiber membrane was evaluated by contact angle measurements using a Contact Angle Measurement Meter (DSA-100, KRŰSS, Germany, with the static sessile drop mode). A 3 μL droplet of DI water was dropped on the dry membrane surface through the micro-syringe with a stainless steel needle. The water droplet image was captured and analyzed for obtaining the water contact angle of the tested membrane. All measurements and experiments were performed at ambient conditions and room temperature. For each membrane sample, 5 measurements of water at different locations on the membrane surface were carried out for attaining the average value of water contact angle.

2.3.5. Measurement of water entry pressure

Water entry pressure was a critical transmembrane pressure of GE-coated PP hollow fiber membrane. The efficient transmembrane pressure of GE-coated PP hollow fiber membrane was determined by water entry pressure measurement. A laboratory-scale microfiltration setup was employed to measure water entry pressure of GE-coated PP hollow fiber membrane, as shown in Fig. 1. The dry membrane samples were cut into pieces of 15 cm length and packed into membrane modules for the water entry pressure measurement. If the transmembrane pressure imposed on GE-coated PP hollow fiber membranes was more than the critical transmembrane pressure, the water droplet would be forced to permeate from the outside to the inside of the GE-coated PP hollow fiber membrane.

2.3.6. Continuous oil-water separation test

The negative pressure dead-end filtration experiments with the GE-coated PP hollow fiber membranes were conducted using a laboratory-scale continuous setup with a vacuum system consisting of a feed reservoir, a vacuum meter, a valve, a kerosene storage tank, and a vacuum pump (SHZ-IIID, China); as shown in Fig. 2. The transmembrane pressure was finely controlled via the pressure controller and ball valve. In this study, the transmembrane pressure was set at –0.09 MPa according to the water enter pressure of the GE-coated PP hollow fiber membranes.

Kerosene was used as a testing liquid to evaluate the GE-coated PP hollow fiber membranes' continuous oil-water separation performance in the negative pressure dead-end filtration experiments. The volume ratio of the kerosene-water mixture was 1:1. For determine if the water is present in permeate, water was dyed by Congo red. Kerosene was not dyed by any dyes.

Each of the negative pressure dead-end filtration experiments was conducted in 2 steps: firstly, the GE-coated PP hollow fiber membrane was packed into membrane module, and then dipped it into oil-water mixture, adjusting and placing it at the oil-water interface; secondly, the GE-coated PP hollow fiber membrane module was mounted with a vacuum system for continuous removal of oils from water surfaces (Fig. 2). The oil flux change was recorded at different time intervals (From 0 to 8 h, time step 30 min). The flux was calculated by following Eq. (3):

$$J = V/(A \times t) \tag{3}$$

where V is the oils flow volume of permeation (L), A is the effective area of membrane (m^2), and t is the filtration time (h).

2.3.7. Reusability of membranes

To evaluate the reusability performance, GE-coated PP hollow fiber membranes were used for continuous kerosene-water separation test for 9 cycles. After each filtration of kerosene-water mixture, the membrane was rinsed and cleaned using ethanol for 15 min to remove the adsorbed kerosene on the surface and internal pore walls of the GE-coated hollow fiber membranes, and then completely dried in the vacuum oven at room temperature for the next filtration. Decline rate was calculated by following Eq. (4):

$$\varepsilon = (F_{i+1} - F_i)/F_i \tag{4}$$

where ε is decline rate, F_i is the stable kerosene flux of GE-coated PP hollow fiber membranes for kerosene-water separation (i = 1,2, 3, 4, 5, 6, 7,8).

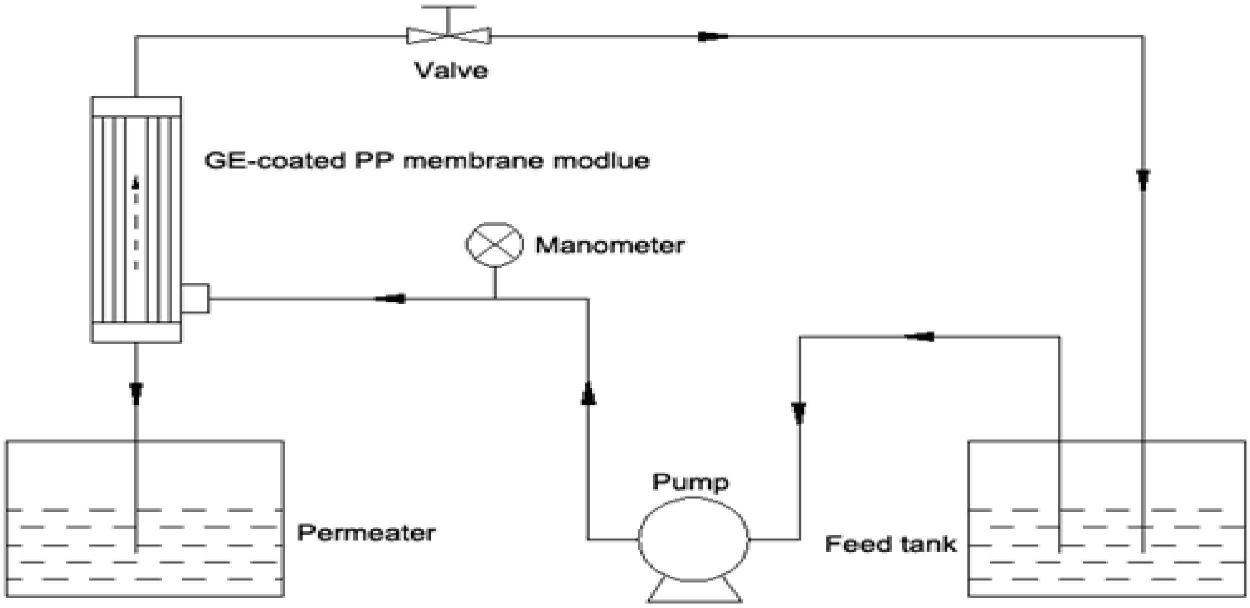

Fig. 1. Schematic diagram for microfiltration experiments.

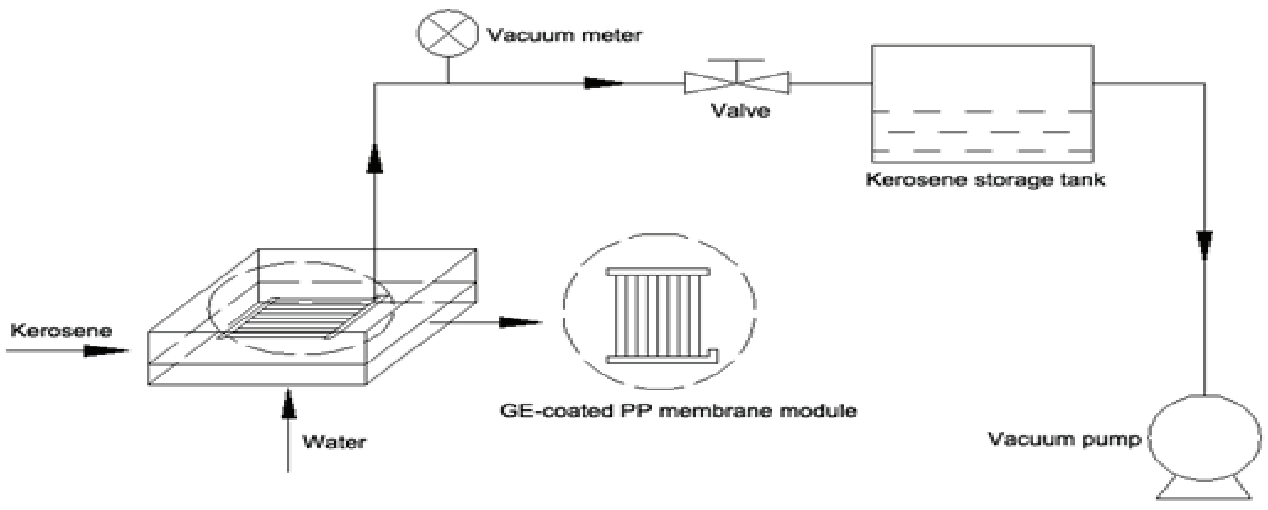

Fig. 2 .The schematic diagram of continuous oil-water separation equipment of GE-coated PP hollow fiber membranes.

Table 1
The coating amount of GE on GE-coated PP hollow fiber membrane

Membrane type	W(g/m^2)
M1	2.24 ± 0.18
M2	4.38 ± 0.21
M3	8.13 ± 0.32
M4	13.16 ± 0.35
M5	13.78 ± 0.34

3. Results and discussion

3.1. Relationship of GE loading and coating time

From Table 1 and Fig. 3, it can be found that GE on GE-coated PP hollow fiber membrane surface dramatically increase with increasing coating time. The color of out surface of the PP hollow fiber membrane change from white to black gradually with increasing coating time. For the out surface color of M1 and M2 is grey white, we think the coating amount of GE on M1 and M2 is not enough to cover the membrane surface completely. It need to load more GE on membrane surface for M1 and M2. On the contrary, GE has totally covered the membrane surface of M3 and M4, and the surface of the white original PP hollow fiber membrane cannot be seen by naked eyes (Fig. 3). It can be seen that some GE pieced off from the surface of M5 (Fig. 3).Originally, a thick GE layer formed on the surface of M5 with longest coating time. However, the GE automatically piece off from the surface of M5 after drying due to the poor adhesion between GE and the membrane surface. It can be used to explain that the amount of GE on M4 and M5 is adjacent. Therefore, the coating time exceed 60 s is not useful. In terms of costs, the preferable coating time is 45 s and the amount of GE on M3 is only8.13 g/m^2. It is an economic method to combine GE with PP hollow fiber membrane.

3.2. Morphology of GE-coated PP hollow fiber membrane

Fig. 4 is the images of M3 before and after hot solvent treatment under different temperatures. These membranes was gently pressed and slid on an empty paper before taking photos. It can be clearly seen that the untreated M3 and 115-M3 treated by hot DMB of 115°C left a black mark on the white paper (Fig. 4 red marks), a sign of GE desquamated, while the 120-M3 and 125-M3 leave nothing. This phenomenon shows that the bonding force between GE and membrane only by the physical adhesion is weak, and GE is easy to be fall off from the PP membrane surface under the external force. Therefore, some measures must be taken to strengthen the combination of GE with PP hollow fiber membrane. The method that using solvent make the PP membrane surface slightly soluble and GE conveniently embed inside the membrane may be workable. But there is no solvents can dissolve PP membrane at room temperature for its good chemical stability. We should treat the PP membrane at appropriate temperatures. From Fig. 4, it can be seen that the treatment of 115°C do not increase the combination of GE with PP hollow fiber membrane. It isn't the suitable temperature. Compare to 120-M3, some surface cracks appear on the surface of 125-M3 due to the higher treating temperature.

Fig. 5a (1) shows that the PP hollow fiber membrane is a kind of homogeneous membrane which has sponge-like pore structure. The outer surface of M0 is smooth (Fig. 5a (3)) and the outer surface of 120-M3 is rough (Fig. 5b (3)). Fig. 5b (3) clearly shows a layer with stacked and folded GE sheets on the GE-coated PP hollow fiber membranes surface. The wettability of membrane surface can be affected by its chemical composition and surface roughness [22]. Irregularly stacked multilayer GE nanosheets comprised the microstructure, whereas folding and agglomeration of GE nanoflakes with few layers comprised the nanostructure [23]. Microstructure and nanostructure formed capillary structure similar to a lotus leaf surface. In addition, the surface tension of the GE is very low, only 46.7 dyn/cm [24], lower than the surface tension of water (72.7 dyn/cm). It is

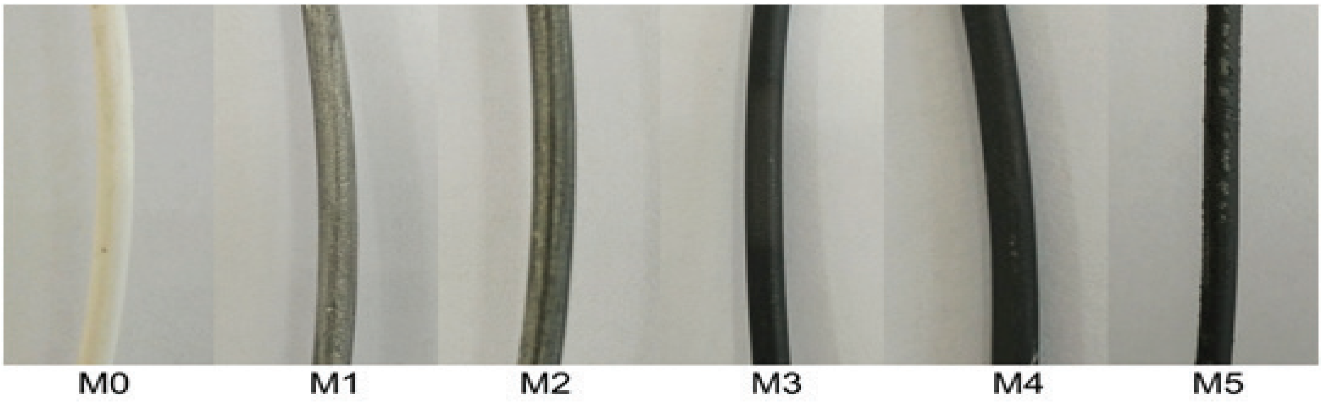

Fig. 3. Images of PP hollow fiber membranes after absorbing GE.

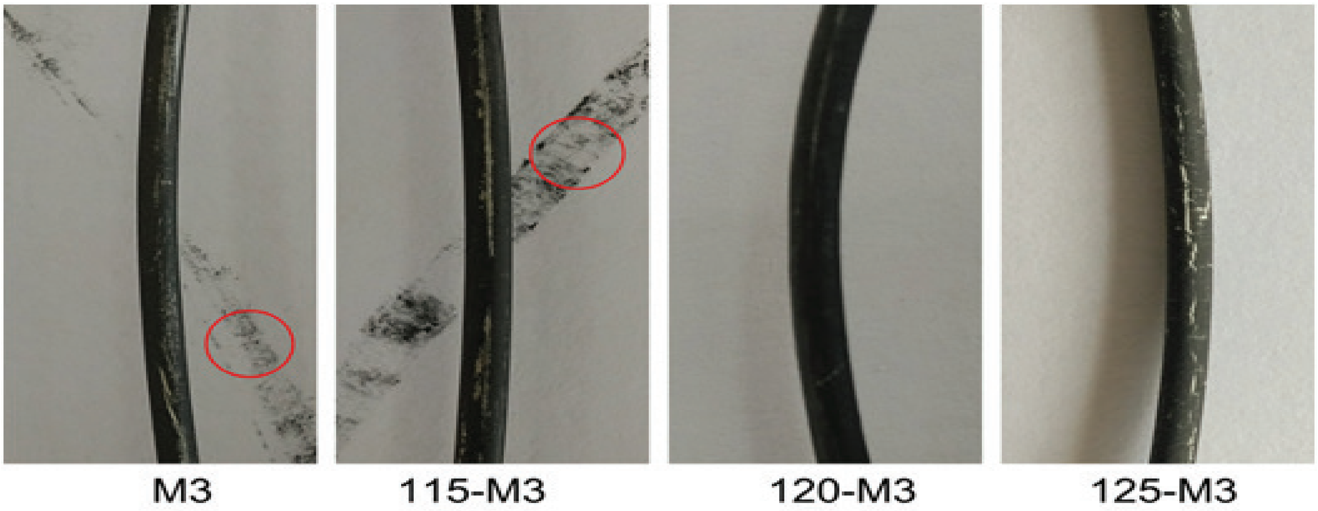

Fig. 4. Images of M3 before and after hot solvent treatment under different temperatures.

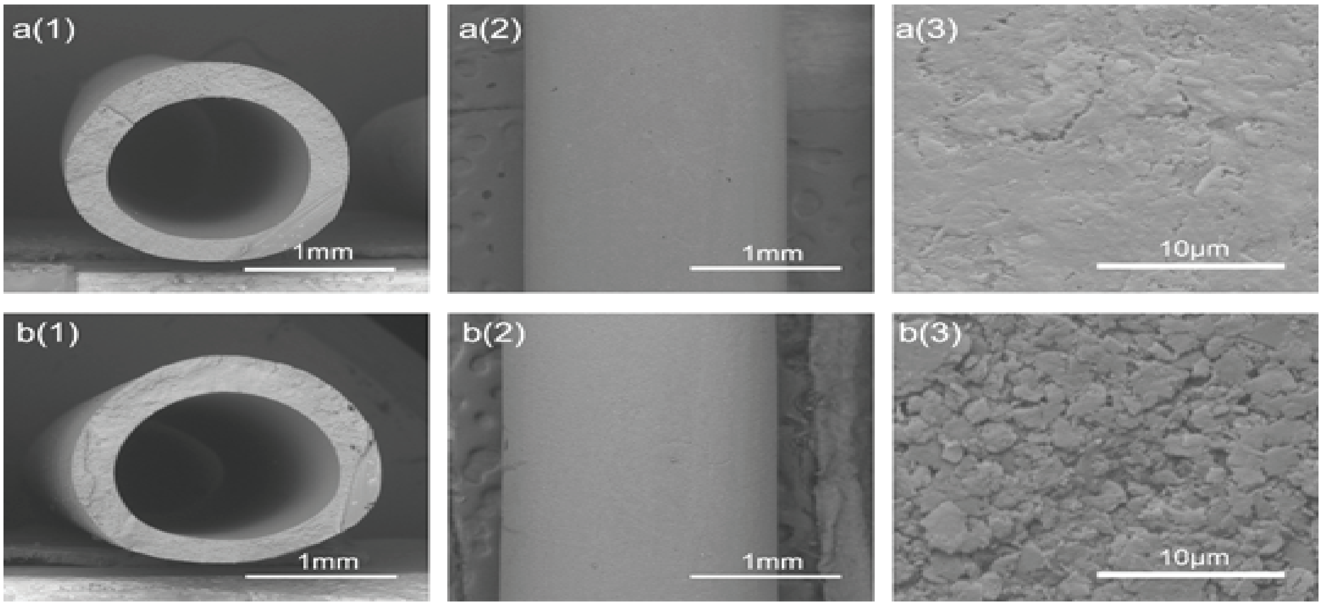

Fig. 5. SEM images of M0 and 120-M3 (a: M0; b: 120-M3; (1) cross-section; (2) outer surface; (3):partial enlargement of outer surface).

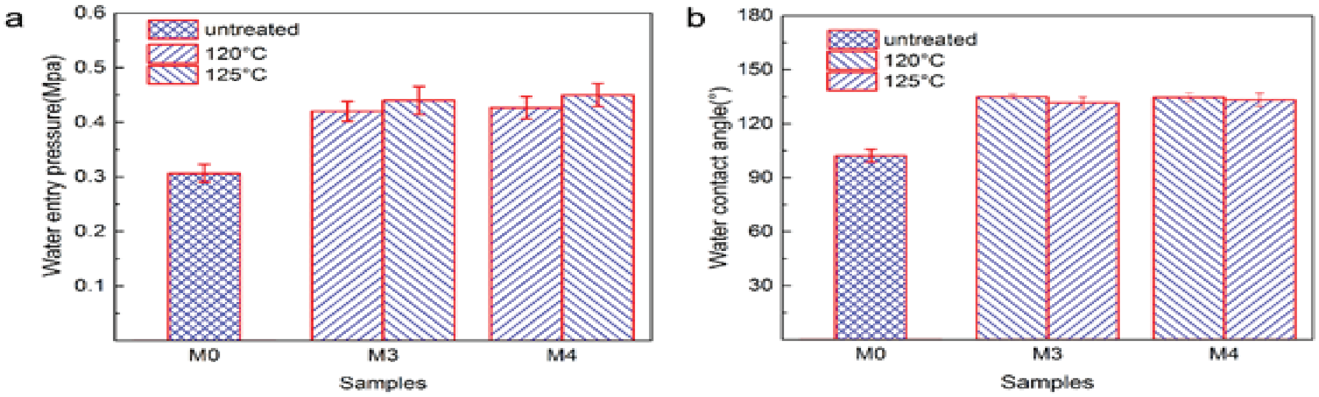

Fig. 6. Water entry pressure and water contact angle of M0, M3 and M4 treated at different temperatures.

Table 2
Characterization of M0, M3 and M4 treated at different temperatures

Samples	Inter diameter(mm)	Outer diameter(mm)	Porosity (%)	Bubble pore size (μm)	Contact angle (°)
M0	1.33 ± 0.01	1.93 ± 0.02	50.93 ± 1.63	0.15	102.22 ± 1.65
120-M3	1.23 ± 0.05	1.87 ± 0.04	40.53 ± 2.12	0.12	134.94 ± 1.43
120-M4	1.24 ± 0.04	1.87 ± 0.05	41.04 ± 2.31	0.12	134.78 ± 2.39
125-M3	1.25 ± 0.06	1.84 ± 0.05	32.51 ± 2.72	0.11	131.57 ± 3.45
125-M4	1.23 ± 0.05	1.85 ± 0.06	31.35 ± 3.03	0.11	133.24 ± 3.78

not easy wetting by water,and the hydrophobic property of PP hollow fiber membrane is increased.

3.3. Membrane surface wetting properties

As shown in Fig. 6, the water entry pressures of GE-coated membrane M3 and M4 after hot DMB treatment are greater than the original M0 without hot DMB treatment. And furthermore, the water entry pressure increases with the increased treating temperatures. The water contact angle of the PP hollow fiber membrane without GE (M0) is 102.2°, which is the smallest of all (Fig. 6b).This can be explained that GE stacked on the outer surface of membrane is hydrophobic and the irregularly stacked multilayer GE lead to the rough membrane surface. Such surface would increase the water contact angle of GE-coated membrane. From Table 2, it can be seen that the bubble pore sizes of GE-coated membrane M3 and M4 after hot DMB treatment are smaller than M0. This may be attributed that the PP membrane surface is slight soluble due to hot DMB and some pores become smaller and even closed. The reduction of bubble pore size and the improvement of water contact angle can well explain the improvement of water entry pressure, as describe in the Young-Laplace equation [25]. The value of water contact angle of the GE-coated PP hollow fiber membranes are close, about 130° (Table 2), and the porosity of the GE-coated PP hollow fiber membrane decreases with increasing treatment temperature. Therefore, 120°C is the optimal processing temperature from the perspective of strengthen the combination between GE and PP hollow fiber membrane and reduce the impact on the properties of PP hollow fiber membrane by hot DMB treatment.

3.4. Continuous oil-water separation performance of GE-coated PP membranes

After 5 min standing, the dyed water isn't found in the permeate liquid collected from the oil-water separation test. The results indicated the membranes completely repelled the water during the 8 h continuous oil-water separation process, accompanied by its hydrophobicity and high water entry pressure. The kerosene fluxes of GE-coated PP hollow fiber membranes are less than the untreated PP hollow fiber membrane. This may be attributed that some pores in the hot solvent treated PP hollow fiber membrane become smaller and even closed, and the porosity of GE-coated PP hollow fiber membranes reduced after hot DMB treatment. From Fig. 7, it can be found that the flux of untreated PP hollow fiber membrane (M0) has no change while the flux change of the GE-coated PP hollow fiber membranes (120-M3, 125-M3, 120-M4) exhibits obvious flux decline during the 8 h kerosene separation process. The reduced porosity of GE-coated PP membranes lead to some oils easily adhered on the surface and internal pore walls. Thus the transfer velocity of kerosene inside of GE-coated PP membrane become slowly and the kerosene flux decreases. The purity of the kerosene filtrate was evaluated by a Karl Fischer analyzer (BYES2000, China). Only 38 ppm and 33 ppm of water, even lower than the moisture content of kerosene before oil-water separation test (53 ppm), was detected in the kerosene filtrate of M0 and 120-M3. The GE-coated PP hollow fiber membrane showed a better oil-water separation efficiency.

As shown in Fig. 7, the kerosene flux of 120-M3 and 125-M3 both exhibits decreased trend. It is notify that the flux of 120-M3 is bigger than 125-M3 .This may be due to higher

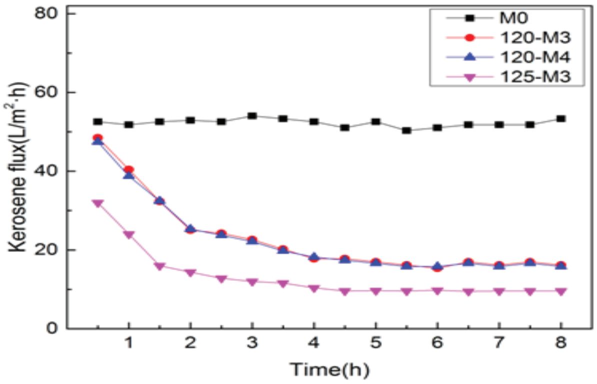

Fig. 7. Kerosene flux of the GE-coated PP membranes from oil-water separation.

processing temperature make the membrane pores smaller, resulting in the flux decreases. The flux of 120-M3 and 120-M4 GE-coated PP hollow fiber membrane is almost the same. The flux don't change with the increased GE, indicated that the GE amount on outer surface of 120-M3 is enough, and 120-M3 was used for evaluating the reusability.

3.5. Reusability of GE-coated PP hollow fiber membranes

Fig. 8 showed the reusability of the GE-coated PP hollow fiber membranes (120-M3) for treating the kerosene-water mixture in 9 cycles. After each separation, the membrane was simply washed with ethanol to recover the flux. From Fig. 8, it could be seen that the stable flux of the GE-coated PP hollow fiber membrane (120-M3) remains16–17 L/m^2 h with increasing cycle times, and no significant decline was observed. All the decline rates were less than 0.1% after 9 cycles, showing a good reusability performance of the GE-coated PP hollow fiber membranes (120-M3).

4. Conclusion

GE coating layer on PP hollow fiber membrane was obtained by the method of dead end filtration. The combination between GE and PP hollow fiber membrane become stronger after a hot solvent treatment. The water contact angle and water entry pressure of the GE-coated PP hollow fiber membranes were higher than M0. GE-coated PP hollow fiber membrane was used for kerosene-water separation through a laboratory-scale continuous setup under –0.09 MPa. The kerosene flux of the GE-coated PP hollow fiber membranes (120-M3, 125-M3, 120-M4) exhibits obvious flux decline compare with the untreated PP hollow fiber membrane (M0) during the 8 h kerosene-water separation process, due to the lower porosity and bubble pore size caused by the hot solvent treatment. To improve the flux of the GE-coated PP hollow fiber membranes, the post-processing of the membranes may be effective. The stable flux of the GE-coated PP hollow fiber membrane remains 16–17 L/m^2 h with increasing cycle times, showing a good reusability performance. Moreover, GE materials have a good adsorption on heavy metal ions [26–27], this GE-coated PP membrane materials may be have potential application removing heavy metal ions.

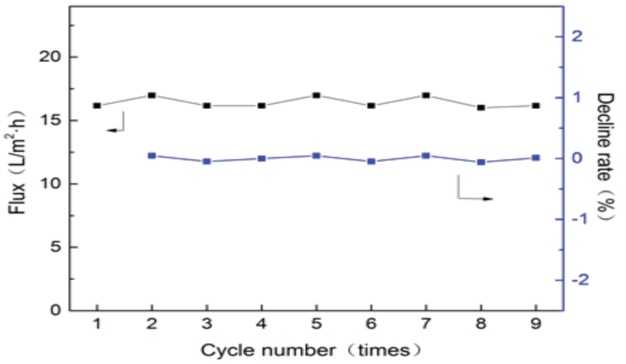

Fig. 8. Change of the flux and decline rate with increasing cycle number of 120-M3.

Acknowledgments

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References

[1] V. Broje, A.A. Keller, Improved mechanical oil spill recovery using an optimized geometry for the skimmer surface. Environ. Sci. Technol., 40 (2006) 7914–7918.
[2] E.B. Kujawinski, M.C.K. Soule, D.L. Valentine, A.K. Boysen, K. Longnecker, M.C. Redmond, Fate of dispersants associated with the deepwater horizon oil spill. Environ. Sci. Technol., 45 (2011) 1298–1306.
[3] H.A. Aziz, M.A. Zahed, M.H. Isa, L. Mohajeri, S. Mohajeri, Optimal conditions for bioremediation of oily seawater. Biores. Technol., 101 (2010) 9455–9460.
[4] H.M. Choi, R.M. Cloud, Natural sorbents in oil spill cleanup. Environ. Sci. Technol., 26 (1992) 772–776.
[5] M.O. Adebajo, R.L. Frost, J.T. Kloprogge, O. Carmody, S. Kokot, Porous materials for oil spill cleanup: a review of synthesis and absorbing properties. J. Porous. Mater., 10 (2003) 159–170.
[6] A. Bayat, S.F. Aghamiri, A. Moheb, G.R. Vakili-Nezhaad, Oil spill cleanup from sea water by sorbent materials. Chem. Eng. Technol., 28 (2005) 1525–1528.
[7] A.L. Ahmad, S. Sumathi, B.H. Hameed, Residual oil and suspended solid removal using natural adsorbents chitosan, bentonite and activated carbon: A comparative study. Chem. Eng. Technol., 08 (2005) 179–185.
[8] S. Suni, A.L. Kosunenc, M. Hautalad, A. Pasilae, M. Romantschuka, Use of a by-product of peat excavation, cotton grass fibre, as a sorbent for oil-spills. Mar. Pollut. Bull., 49 (2004) 916–921.
[9] Q.F. Wei, R.R. Mather, A.F. Fotheringham, R.D. Yang. Evaluation of nonwoven polypropylene oil sorbents in marine oil-spill recovery. Mar. Pollut. Bull., (2003) 780–783.
[10] H. Li, L. Liu, F. Yang, Hydrophobic modification of polyurethane foam for oil spill cleanup. Mar. Pollut. Bull., 64 (2012) 1648–1653.
[11] M. Hemmatia, F. Rekabdara, A. Gheshlaghia, A. Salahib, T. Mohammadic, Effects of air sparging, cross flow velocity and pressure on permeation flux enhancement in industrial oily wastewater treatment using microfiltration. Desal. Water. Treat., 39 (2012) 33–40.

[12] Y. Zhao, J. Zhong, H. Li, N. Xu, J. Shi, Fouling and regeneration of ceramic microfiltration membranes in processing acid wastewater containing fine TiO_2 particles, J. Membr. Sci., 208 (2002) 331–341.

[13] J. Cui, X. Zhang, H. Liu, S. Liu, K.L. Yeung, Preparation and application of zeolite/ceramic microfiltration membranes for treatment of oil contaminated water, J. Membr. Sci., 325 (2008) 420–426.

[14] M. Ebrahimi, D. Willershausen, K.Sh. Ashaghi, L. Engel, L. Placido, P. Mund, P. Bolduan, P. Czermak, Investigations on the use of different ceramic membranes for efficient oil-field produced water treatment. Desalination, 250 (2010) 991–996.

[15] F.L. Hua, Y.F. Tsang, Y.J. Wang, S.Y. Chan, H. Chua, S.N. Sin, Performance study of ceramic microfiltration membrane for oily wastewater treatment. Chem. Eng. J., 2007 (2007) 169–175.

[16] M. Ebrahimi, K.S. Ashaghi, L. Engel, D. Willershausen, P. Mund, P. Bolduan, P. Czermak, Characterization and application of different ceramic membranes for the oil-field produced water treatment. Desalination, 245 (2009) 533–540.

[17] J. Rafiee, M.A. Rafiee, Z.Z. Yu, N. Koratkar, Superhydrophobic to superhydrophilic wetting control in graphene films. Adv. Mater., 22 (2010) 2151–2154.

[18] H.Y. Sun, Z. Xu, C. Gao, Multifunctional, ultra-fly weight, synergistically assembled carbon aerogels, Adv. Mater., 25 (2013) 2554–2560.

[19] H. Bi, X. Xie, K. Yin, Yilong Zhou, S. Wan, L.B. He, F. Xu, F. Banhart, L.T. Sun, R.S. Ruoff, Spongy graphene as a highly efficient and recyclable sorbent for oils and organic solvents. Adv. Funct. Mater., (2012) 4421–4425.

[20] D.D. Nguyen, N.H. Tai, S.B. Lee, W.S. Kuo, Superhydrophobic and superoleophilic properties of graphene-based sponges fabricated using a facile dip coating method. Energ. Environ. Sci., 5 (2012) 7908–7912.

[21] S. H. Tabatabaei, P.J. Carreau, A. Ajji, Microporous membranes obtained from polypropylene blend films by stretching. J. Membr. Sci., 325 (2008) 772–782.

[22] J. Rafiee, M.A. Rafiee, Z.Z. Yu, N. Koratkar, Superhydrophobic to superhydrophilic wetting control in graphene films. Adv. Mater., 22 (2010) 2151–2154.

[23] X. Zhang, S.H. Wan, J.B. Pu, L.P. Wang, X.Q. Liu, Highly hydrophobic and adhesive performance of graphene films. J. Mater. Chem., 21 (2011) 12251–12258.

[24] Z. Niu, J. Chen, H.H. Hng, X. Chen, A leavening strategy to prepare reduced graphene oxide foams. Adv. Mater., 24 (2012) 4144–4150.

[25] L.R. Fisher, P.D. Lark, An experimental study of the wash burn equation for liquid flow in very fine capillaries. J. Colloid. Interface. Sci., 69 (1979) 486–492.

[26] S.T. Yang, Y.L. Chang, H.F. Wang, et al., Folding/aggregation of grapheme oxide and its application in Cu^{2+} removal, J. Colloid Interface Sci., 351 (2010) 122–127.

[27] V. Chandra, J. Park, Y. Chun, et al., Water-dispersible magnetite-reduced grapheme oxide composites for Arsenic removal. ACS Nano, 4 (2010) 3979–3986.